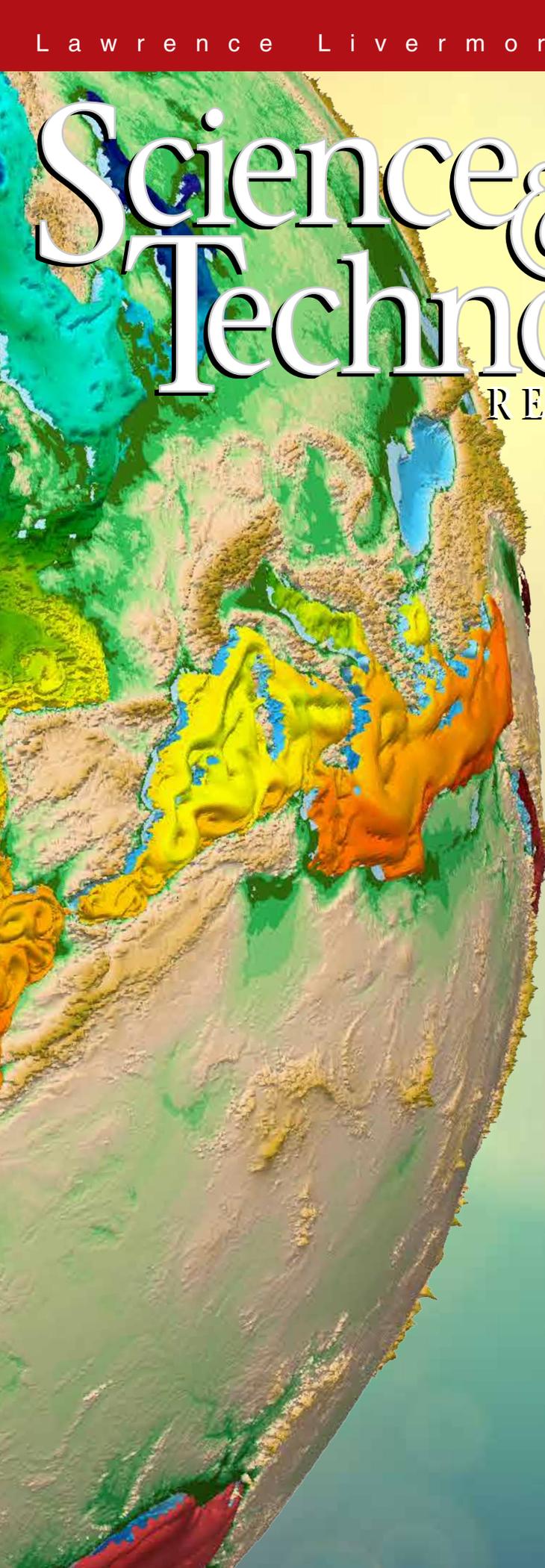


December 2017



Science & Technology

REVIEW

Simulating the Earth System

Also in this issue:

Carbon Capture Breakthrough

Water in Earth's Mantle?

A Revolution in Optics

About the Cover

Advances in supercomputing capabilities and nuclear weapons research have contributed to the evolution of climate modeling at Lawrence Livermore, as the article beginning on p. 4 describes. For instance, in the 1960s former Manhattan Project researcher Cecil “Chuck” Leith created the world’s first global atmospheric model. Atmospheric chemistry modeling helped study a large hole in the ozone layer, while atmospheric release modeling helped to safeguard citizens after catastrophes such as Chernobyl’s nuclear accident. Building on these decades of achievements, climate models continue to advance today. The cover shows a simulation from the Energy Exascale Earth System Model, which will run on the most advanced supercomputers yet and produce results of unprecedented resolution.



Cover design: Alexandria Diaz

About S&TR

At Lawrence Livermore National Laboratory, we focus on science and technology research to ensure our nation’s security. We also apply that expertise to solve other important national problems in energy, bioscience, and the environment. *Science & Technology Review* is published eight times a year to communicate, to a broad audience, the Laboratory’s scientific and technological accomplishments in fulfilling its primary missions. The publication’s goal is to help readers understand these accomplishments and appreciate their value to the individual citizen, the nation, and the world.

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Metal Ink Reinvents Three-Dimensional Printing

Lawrence Livermore researchers, in collaboration with Worcester Polytechnic Institute, have developed a new three-dimensional (3D) printing process called direct metal writing, which overcomes some of the limitations faced by 3D printing with fine metal powder fused together by lasers. Parts produced using selective laser melting and other powder-based metal techniques often have gaps or defects caused by various factors.

Instead, direct metal writing uses a metal ingot that is heated until it reaches a semi-solid state, in which solid metal particles are surrounded by liquid metal. The pastelike metal can then be forced through a nozzle. To achieve the required flow, researchers precisely control the temperature of the metal ink and how it is stirred. The process has also allowed the printing of self-supporting metal 3D structures, which had never been achieved before. The research appears in the February 27, 2017, edition of *Applied Physics Letters*.

“We’re in new territory,” states Wen Chen, a Livermore materials scientist and lead author of the paper. “We have developed a new, advanced metal additive manufacturing technique that people aren’t aware of yet. I think many researchers will be interested in continuing this work and expanding it into other alloys.” The technique uses a bismuth–tin mixture, which has a relatively low melting point of 300°C. Further work is needed to achieve higher printing resolution with more industry-relevant metals having higher melting points, such as aluminum and titanium. The research was supported by the Laboratory Directed Research and Development Program.

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A Rapid Bacterial Detection Kit

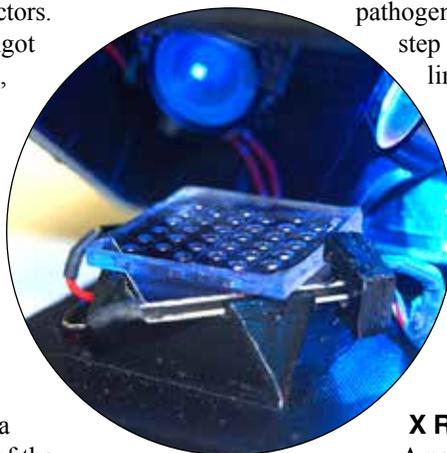
An urgent need exists for rapid bacteria detection in rural areas and developing countries, among other applications. The current standard for bacterial identification is to isolate and grow the species in an assay, which can take hours to weeks. However, Livermore scientists, in collaboration with the University of Wisconsin at Madison, have developed a diagnostic kit that can assess up to 16 different diseases in roughly one hour. Designed to be low-cost, portable, and easy to use, the kit (shown in the image above) is about the size of a shoebox and runs on 9-volt batteries. A disposable sample container called a B-chip (bacteria-detection chip), which contains 16 microchambers, is loaded into the kit, whose B-chip reader detects pathogens by performing a recombinase polymerase amplification (RPA) assay.

Livermore principal investigator Tuan Nguyen explains, “RPA reactions are sensitive, specific, and rapid and operate at a constant, low temperature, which minimizes power consumption

and simplifies heating and power handling.” The researchers tested the kit against a panel of bacterial infections called ESKAPE (*Enterococcus faecium*, *Staphylococcus aureus*, *Klebsiella pneumoniae*, *Acinetobacter baumannii*, *Pseudomonas aeruginosa*, and *Enterobacter*), which often escape the effects of many antibiotics.

Nguyen says, “Making progress toward timely and accurate pathogen identification in an infection is the critical first step in effective patient care, especially in resource-limited environments, enabling proper usage of antibiotics to mitigate the growing emergence of antibiotic resistance.” Appearing in the February 2017 issue of *Applied and Environmental Microbiology*, the research was funded by the Department of Defense and the Bill and Melinda Gates Foundation, with support from the National Science Foundation.

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X Rays from Laser-Induced Plasma Wakes

A new method of generating x rays is capable of probing the size, density, pressure, and composition of highly transient states of matter, as well as studying the dynamics of high-energy-density plasmas and warm dense matter. The method was developed by a team of Livermore researchers led by physicist F elicie Albert in collaboration with the University of California (UC) at Los Angeles, SLAC National Accelerator Laboratory, Lawrence Berkeley National Laboratory, UC Berkeley, and the University of Lisbon in Portugal.

In research described in the March 31, 2017, edition of *Physical Review Letters*, a kilojoule-class picosecond laser was focused into a plasma to create a plasma wakefield. Each pulse from the laser overlaps with numerous plasma wake periods, and the resulting self-modulation and channeling accelerate electrons in the wake up to energies of 200 megaelectronvolts, causing the electrons to emit betatron x rays. This small-divergence broadband source of radiation can be used as a backlight to probe various samples.

To investigate betatron x-ray emission at the intensities and pulse durations relevant to larger scale laser facilities, such as the Advanced Radiographic Capability laser at the National Ignition Facility, the researchers conducted an experiment on Livermore’s Titan Laser. Betatron x-ray radiation driven by much longer, picosecond-duration laser pulses was observed. These results showed that the new radiation source holds great promise for applications at international large-scale laser facilities, where the source could be used for x-ray radiography and the phase-contrast imaging of laser-driven shocks, absorption spectroscopy, and opacity measurements.

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Advances Benefit Multiple Missions

LAURENCE Livermore recently celebrated its 65th anniversary. At such an exciting milestone, we naturally reflect on our past and what got us here. The application of high-performance computing to advance the frontiers of science is an important part of our past, as well as our future. The intensive use of leading-edge computing began as soon as the Laboratory's doors first opened and has since allowed us to stay at the forefront of science and technology.

Computer simulations were vital in our early breakthroughs in nuclear weapons design and today are a cornerstone of sustaining the nation's aging nuclear weapons stockpile. Our complex physics and engineering models—validated by data from experiments—are used to perform integrated experiments of weapons performance on some of the world's most powerful supercomputers.

The same approach to tackling difficult national challenges is pervasive in Livermore's research in other application areas, including efforts to understand human influences on the environment. The article starting on p. 4 describes the Laboratory's long history of work on atmospheric science and climate modeling. Our first efforts tested whether simulations of the fundamental physics equations governing Earth's atmosphere could reproduce weatherlike patterns. They did. Since the early studies, modeling capabilities have advanced along with the power of the computers themselves, and Livermore scientists subsequently addressed issues such as the effects of atmospheric nuclear tests, atmospheric ozone, nuclear winter, and the fallout from nuclear and other toxic-material accidents.

The increasing number and complexity of climate models across the globe led to the Program for Climate Model Diagnosis and Intercomparison (PCMDI), which was founded at the Laboratory in 1989. Engaging international collaborators, PCMDI did pioneering analysis and evaluation of climate models and actual observed data over the decades to continually improve the performance of climate models. In fact, PCMDI's work contributed to the co-award of the 2007 Nobel Peace Prize to the Intergovernmental Panel on Climate Change.

A multilaboratory effort launched by the Department of Energy's Office of Science in 2014, the Energy Exascale Earth

System Model (E3SM) takes advantage of next-generation high-performance computers. E3SM promises to yield unprecedented understanding of the Earth system by performing simulations to help address energy-related questions critical to the nation—not just on global scales but even down to regions as small as 1 square kilometer.

As with our nuclear weapons efforts, we seek data to corroborate, validate, and continually improve the fidelity and predictive capability of simulations and the underlying models. Gathering data is an enormous international effort. Many articles in *S&TR* in recent years have highlighted our contributions to these international data-gathering efforts, such as the Earth System Grid Federation. In addition, Livermore possesses advanced tools, such the Center for Accelerator Mass Spectrometry, used by climate scientists around the world to better understand the cycling of carbon among the Earth's soil, oceans, and atmosphere. We are interested in our planet's climate history and what changes have transpired in recent decades.

We are also developing innovative technologies to capture carbon and mitigate warming, as described in the highlight on p. 12. The Laboratory's expertise in additive manufacturing (AM) was a critical part of this development—exemplifying, as with the nuclear weapons–climate link, that the science, technology, and understanding necessary to address one Laboratory mission often cascade from, overlap with, and benefit other missions. Among many other advances, AM is yielding revolutionary methods to manufacture precision optics and laser cavity amplifiers, as described in the highlight on p. 20. Capabilities found in few places in the world, such as the Laboratory's nanoscale secondary ion mass spectrometer instrument, allow us to unlock mysteries of water's presence on our planet by submicrometer examination of minerals from deep inside Earth's mantle, as described in the last highlight.

In the pages of this issue, I am pleased to share with you these interconnections among application areas of deep capabilities in modeling, simulation, and computing, as well as in precise and exquisite manufacturing and instrumentation.

■ Patricia Falcone is Deputy Director for Science and Technology.



Smoke from the 2016 Soberanes Fire in Monterey County, California—the costliest wildfire up to that time—begins to block out the Milky Way. Climate change makes droughts more likely and such fires more frequent and larger in scale. (Photo by Li Liu, M.D.)

The Atmosphere around **CLIMATE MODELS**

Supercomputers, the laws of physics, and Lawrence Livermore's nuclear weapons research all interact to advance atmospheric science and climate modeling.

SINCE the 1960s, computer models have been ensuring the safe return of astronauts from orbital and lunar missions by carefully predicting complicated spacecraft trajectories. A slight miscalculation could cause a craft to zoom past the Moon or Earth and become lost in space, or approach too steeply and face an equally disastrous outcome. Bruce Hendrickson, Livermore's associate director for Computation, points out, "In the 1960s, scientists and engineers put people on the Moon with less computing

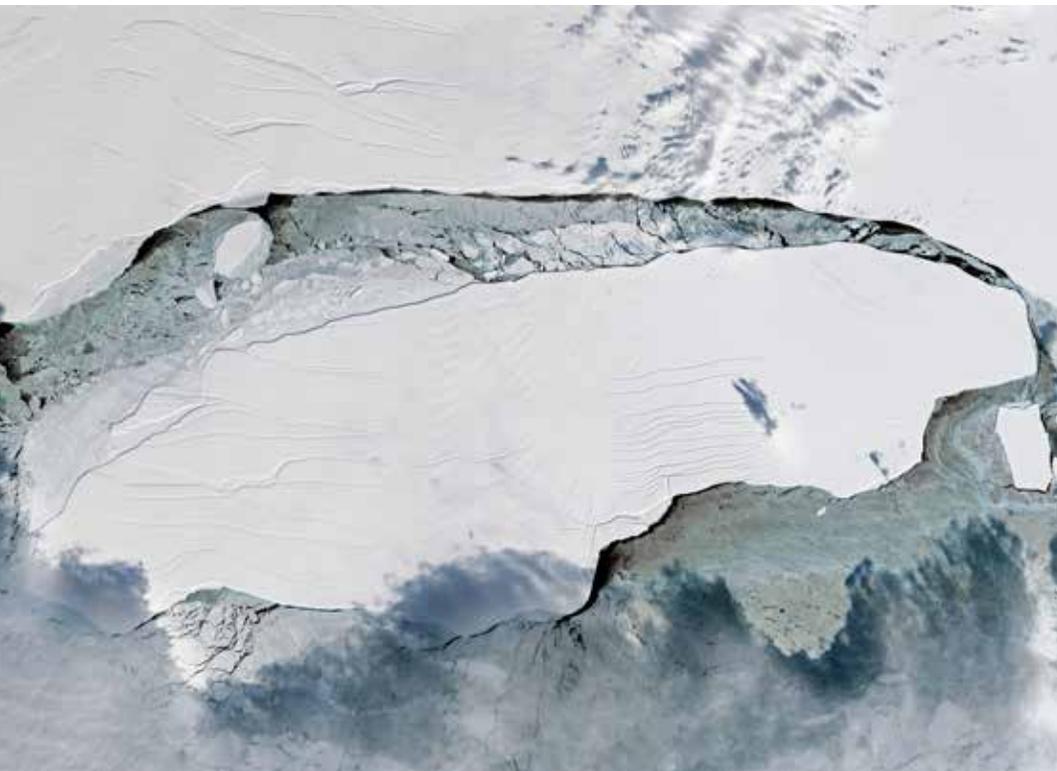
power than we carry in our pockets now, whereas today's advanced computers allow us to study phenomena vastly more complex than orbital dynamics." That computational power offers unprecedented insight into how the physical world works, providing details about phenomena that would be infeasible to study with physical experiments. At Lawrence Livermore, numerical models running on high-performance computers are a vital part of research in many programs, including stockpile stewardship and climate studies.

In fact, Livermore's climate models trace their origins to the Laboratory's initial development of codes to simulate nuclear weapons. Hendrickson states, "Our primary mission is nuclear weapons design, which has required us to create unique computational capabilities. These capabilities have also been applied to other national needs, including modeling the atmosphere and the rest of the climate system."

Over the years, advances in scientific understanding and increased computational

power have resulted in higher fidelity climate models that are more representative of the real world. These computationally intense simulations have also helped shake down and benchmark subsequent generations of the Department of Energy's (DOE's) supercomputers before the machines transition to classified work. "Climate simulation is an application that can consume the whole machine and put it through its paces in a very demanding way," explains Hendrickson. "The simulations touch every part of the computer." (See *S&TR*, July/August 2015, pp. 3–14.)

On July 12, 2017, a 5,801-square-kilometer piece of the Larsen C ice shelf broke away from Antarctica, as shown in the satellite image. The Energy Exascale Earth System Model (E3SM) is one of the first to simulate the movement and evolution of glaciers and ice sheets. (Image courtesy of NASA.)



First Atmospheric Animation

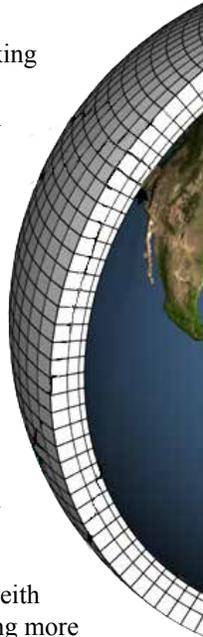
From its inception, the Laboratory pursued numerical approaches to solving problems using cutting-edge computer systems. "Livermore went all-in with computers," says Glenn Fox, associate director for Physical and Life Sciences. "When the Laboratory's doors opened, the first big procurement was a state-of-the-art computer." The room-sized Univac-1 had 5,600 vacuum tubes and 9 kilobytes of memory and ran at a speed of 1,000 floating-point operations per second (flops). In 2018, Livermore's Sierra supercomputer will use more than 1 million microprocessors to achieve a speed of 150 petaflops—150 trillion times faster than the Univac-1.

Even in the Laboratory's early days, researchers understood that the same computational approaches for simulating nuclear weapons could be applied to better simulate evolution of the weather and

for applications such as tracking releases of radioactive and other hazardous materials. In the late 1950s, Livermore scientist Cecil "Chuck" Leith developed one of Livermore's first-ever numerical models capable of simulating the hydrodynamic and radiative processes in a thermonuclear explosion. Recognizing fundamental similarities in the underlying equations and interested in demonstrating what could be achieved with more powerful computing, Leith turned his attention to creating more comprehensive weather system models.

Michael MacCracken, a now-retired climate scientist who headed Livermore's atmospheric and geophysical sciences division from 1987 to 1993, came to the Laboratory as one of Leith's graduate students. MacCracken says, "Using the most advanced computers available in the early 1960s, Leith developed an atmospheric model that was way ahead of its time." Leith's Livermore Atmospheric Model (LAM) divided the atmosphere into a three-dimensional (3D) mesh with six vertical layers and a horizontal grid with five-degree intervals in latitude and longitude. LAM was the world's first global atmospheric circulation model that calculated temperature, winds, humidity, clouds, precipitation, the day-and-night cycle, and weather systems around the globe, all starting from first-principles equations for the conservation of mass, momentum, energy, and water vapor. Leith also created the first animation of atmospheric modeling results by coloring photographs of a black-and-white video screen and stitching them together into a film.

Leith's atmospheric work also benefited other Livermore programs. For example,





Climate models divide Earth into a grid with vertical and horizontal intervals. The smaller the intervals, the finer the grid, and the better the resolution of the model—that is, the greater detail the model can produce. (Image courtesy of the National Oceanic and Atmospheric Administration.)

to these efforts, atmospheric chemistry models were also developed. The first such model contributed to a successful plan to limit rising concentrations of photochemical smog in the San Francisco Bay Area. The second model simulated stratospheric chemistry and was used to calculate the impact of a proposed fleet of supersonic transport aircraft on stratospheric ozone. This modeling also investigated the potential for ozone depletion from atmospheric nuclear testing back in the early 1960s and the much larger depletion that would result from a global nuclear war with megaton-yield nuclear weapons.

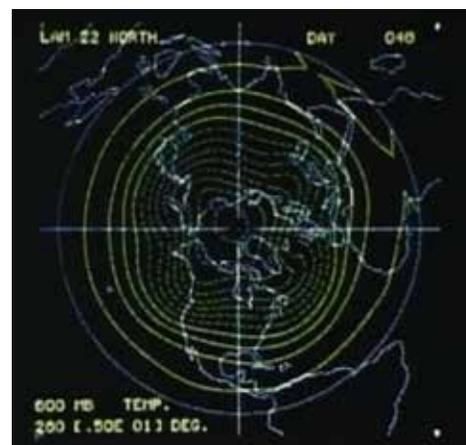
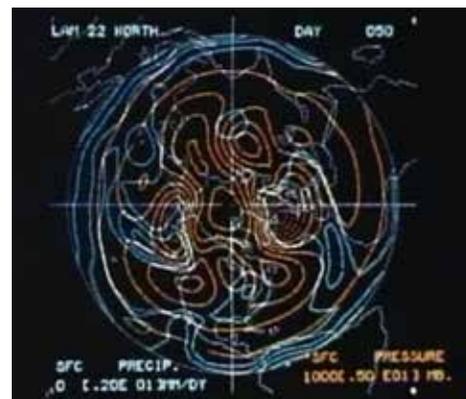
his study of atmospheric turbulence led to a better understanding of how to represent turbulence and turbulent flows. MacCracken adds, “Although simulations of astrophysics, plasma physics, and nuclear weapons address different temperatures, pressures, and timescales, it’s all the same basic physics. So computational advances in one area benefit the others and vice-versa.”

Ozone and Nuclear Winter

As environmental awareness rose in the late 1960s, Laboratory programs began to address regional and global environmental problems. Derived from LAM, an early climate model developed by MacCracken was used to analyze hypotheses about the causes of ice age cycles, the effects of volcanic eruptions and changes in land cover, and the consequences of changes in atmospheric composition. The pioneering LAM would eventually lead to the global climate models that today also encompass interactive representations of the oceans, land surfaces, ice masses, and biological activity in the oceans and on land. Parallel

When chlorofluorocarbon (CFC) emissions from aerosol spray cans, refrigerators, and other sources came under scrutiny in the 1970s, the stratospheric chemistry model was applied to evaluate the ozone depletion potential and develop a metric for calculating depletion that was later used in the Montreal Protocol to regulate CFC emissions. After restrictions were put in place in 1987, growth of the continent-size hole in the ozone layer slowed, and after further international agreements, it eventually stopped growing and began to slowly shrink.

In the mid-1980s, famed astrophysicist Carl Sagan and others suggested the specter of a “nuclear winter”—that the blasts and fires from a global nuclear war could loft enough smoke and other matter into the atmosphere to obscure sunlight for months, causing a global vegetation die-off and a winterlike cooling of the entire planet that could kill billions of people. In 1945, before he cofounded Lawrence Livermore



The Livermore Atmospheric Model (LAM), developed by Cecil “Chuck” Leith in the 1960s, was the first-ever global climate model to be animated. Shown are screen captures of runs for pressure and precipitation (top) and temperature (bottom).

and later became its director from 1958 to 1960, Edward Teller had made the critical determination at Los Alamos that a nuclear explosion would not ignite the atmosphere. Now he questioned the severity of a nuclear winter. Climate scientist Curt Covey, who retired from Livermore in 2017, remembers Teller saying, “At Livermore, we have the best computers. Surely we can do the best job in simulations.” In response, Livermore used its modeling capabilities to investigate the global effects of nuclear winter and found that although significant cooling

would occur depending on the amount of smoke lofted, the effects would be less severe than initially conjectured.

Building on these wide-ranging activities, Livermore was well positioned to simulate and better understand the effects on the climate of increasing concentrations of carbon dioxide (CO₂) and other greenhouse gases. Fox notes, “Although assessing the impact of human activities on the environment was not part of the Laboratory’s original charter, as our capabilities developed, we stepped into a broader program that has played an important role for the country.”

Chernobyl and Tracking Releases

In 1986, the worst nuclear accident in history occurred at the Soviet Union’s

Chernobyl power plant in Ukraine. A partial meltdown of the reactor’s core resulted in a massive explosion and open-air fires that belched radioactive material into the atmosphere for days. Livermore’s National Atmospheric Release Advisory Center (NARAC) had been created by DOE nearly a decade earlier as an emergency response asset and was part of DOE’s 1979 response to the radioactive release at the Three Mile Island reactor in Pennsylvania. Immediately after the Chernobyl accident, NARAC worked with subject-matter experts both inside and outside the Laboratory, quickly connecting its local and regional dispersion models to global meteorological models to estimate where the plume and fallout from Chernobyl would spread.

The models, validated with measurements from different countries, helped to provide a better understanding of the impacts of the release and possible protective measures. This included analysis of the potential threats to the milk supply.

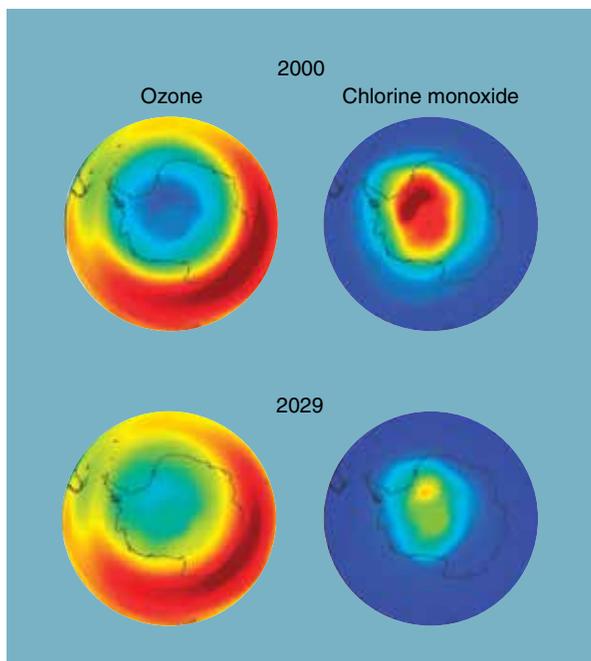
After Chernobyl, NARAC’s responsibilities were expanded to a global scale to better safeguard the nation and the world. Responses to many national and international incidents notably include the 2011 power plant accident in Fukushima, Japan. Today, NARAC is expanding its high-resolution atmospheric and transport models to span spatial scales from the worldwide transport of radiological materials to dispersion down city streets from, say, a radiological dispersal device or an accident at a chemical plant. These models incorporate highly resolved terrain and meteorological information and are used to prepare for a

wide range of release scenarios, including large fires or chemical spills, incidents involving weapons of mass destruction, and nuclear power plant failures. Lee Glascoe, program leader for NARAC, says, “When we are alerted to a hazardous release, we work quickly with DOE using NARAC’s atmospheric modeling capabilities to provide decision makers with predictions of hazards associated with the plume dispersal to help protect workers and the public.”

Climate Model Intercomparisons

Over the decades, computational advances have allowed more components of the climate system to be combined into a single model. Previously, combining components such as the atmosphere, land surfaces, oceans, sea ice, aerosols, and the carbon cycle into one model was far too complex. In 1989, Livermore took the lead in an international program designed to evaluate and learn from the increasing number of climate models being developed by leading scientific organizations around the world. This effort, the Program for Climate Model Diagnosis and Intercomparison (PCMDI), was announced in a press release by Bruce Tarter, then associate director for Physics and later Laboratory director from 1994 to 2002. Tarter stated, “The greenhouse effect is of tremendous global concern. It is essential that the policymakers in the U.S. and internationally have the necessary tools to address it. Our new program will enable us to improve the scientific tool that is of extraordinary value in this effort—the computer model.” (See *S&TR*, June 2012, pp. 4–12.)

Climate models are grounded in the laws of physics, and their simulations of the historical climate are carefully compared to available global observations. This grounding allows researchers to assess many kinds of “what if” climate change scenarios. Tom Phillips has worked as a PCMDI climate scientist for decades and recognizes that



An atmospheric chemistry model jointly developed by Livermore and NASA predicts recovery of the ozone hole between 2000 and 2029. The left-hand panels show the extent of the ozone hole (blue shows minimum ozone), while the right-hand panels show the amount of ozone-destroying chlorine monoxide (peaking in red). Actual data (not shown) confirmed that once steps to reduce ozone-depleting gases were taken, the hole in the ozone stopped growing and began shrinking.

the complexity of climate models can make them difficult to understand, which in turn has led to criticism. For instance, climate scientists have been accused of tweaking the models to produce desired outcomes. Phillips denies the claim, explaining, “We look at the whole system as manifested in different aspects, such as the variation in global temperature, the hydrological cycle, and atmospheric circulation. Even if it were possible to tweak parameters to achieve specific results, the tweak would affect other results, making it very apparent that something was amiss.” Parameters in the models are deeply embedded in the very equations describing physical processes, with values set according to the physics being represented. Modeling results—say, rainfall sensitivity to CO₂—emerge only after the equations have been solved over the range of time covered by the models. Furthermore, results must be consistent with extensive observed data.

For almost three decades, PCMDI has been closely examining and comparing the results of climate models with observed changes in the climate system. If climate model results differ from observations or other models, scientists use this difference as an opportunity for learning. Ongoing testing and intercomparison can thus lead to improvement of all models. Although differences in modeling approaches will lead to some degree of variation among climate models and differences with normal variation of weather, multiple runs from multiple models usually reveal consistent trends when the results are combined into an ensemble.

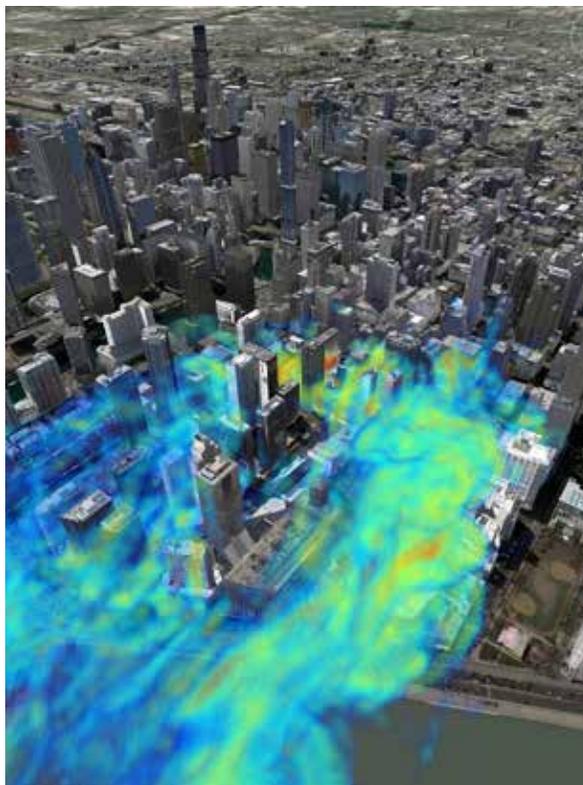
Climate scientist Céline Bonfils, who focuses on hydrological effects such as aridity, confirms that climate models are performing quite well, adding, “The big picture is relatively well understood in terms of the global scale. For instance, the climate models already accurately simulate winter storm tracks in mid-latitudes, monsoon systems, and arid lands

in subtropics. As the world warms, wet regions are tending to become wetter and dry regions drier. What we are doing now is trying to understand the details at much finer levels, on regional scales. People care about what’s happening in their backyard. They also want to know to what extent human-induced climate change might have made Hurricanes Harvey, Irma, and Maria more destructive than previous hurricanes.”

PCMDI has been a major contributor to all five assessment reports by the Intergovernmental Panel on Climate Change (IPCC). After the fourth assessment, more than 40 Livermore researchers were recognized when the IPCC was co-awarded the 2007 Nobel Peace Prize for its efforts to “build up and disseminate greater knowledge about man-made climate change, and to lay the foundations for the measures that are needed to counteract such change.”

Models Meet Supercomputers

In the late 1980s, as the Cold War ended, Laboratory scientists and engineers looked for wider application of their expertise in nuclear weapons modeling and other simulations. Some researchers shifted their careers to climate modeling. Then, in 1996, when the Comprehensive Nuclear-Test-Ban Treaty ended underground testing, science-based stockpile stewardship was born. The modeling of weapons in great detail as they age is central to stockpile stewardship, and the need arose to push even harder on the boundaries of supercomputing, resulting in machines of incredible power. Behind these supercomputers is a small army of computer scientists who develop computer codes used to safeguard the nuclear weapons stockpile, as well as codes employed in climate research. Computer scientist Dean Williams explains, “You cannot use the actual Earth as an experiment. You cannot double or triple the amount of greenhouse gases in



An atmospheric release simulation from Livermore’s National Atmospheric Release Advisory Center shows how a hazardous plume could disperse through streets and flow around buildings. This sophisticated and validated atmospheric model can resolve to the meter scale. The system is being developed to launch on short notice in an emergency to provide responders with actionable information needed to protect people from plume exposure.

the atmosphere to see what happens to the planet. That's an impossible option. The only way we can investigate what would happen is by using computer simulations. We simulate nuclear tests. We simulate how airplanes fly. We've shown this works for complex systems, with close agreement between simulations and observations. If we can do these things, why not climate? The same scientific approach and fundamental physics principles apply to all."

The principal investigator and chair of the Earth System Grid Federation (ESGF), Williams has spent almost 30 years working with climate data. ESGF is a massive data-management system that allows researchers from all over the world to securely store and share models, analyses, and results, along with observational data from satellites and other scientific sources. (See *S&TR*, January/February 2013, pp. 4–11.) Williams says, "As computer scientists, we interface with climate scientists. We also work with the hardware, networking, and other software application teams. When I'm talking about climate models and moving around petabytes of data, I'm dealing with ESGF. We interface with the modelers because they're the ones running the models. We really have to understand the terminology and the science behind

the models so that we can code them and give the researchers useful results." This teamwork also helps spread knowledge about complex modeling approaches and lessons learned throughout the Laboratory's programs.

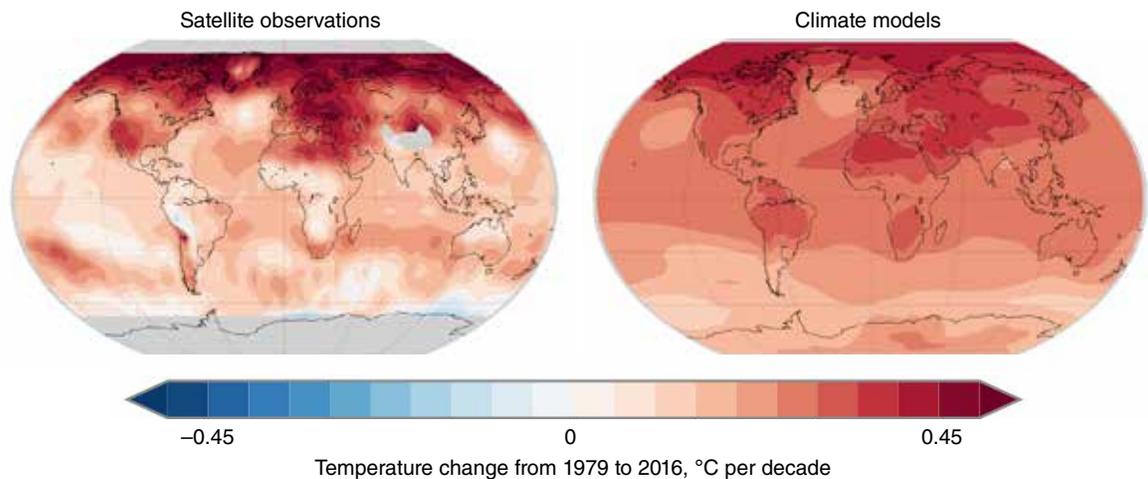
Connecting the Dots

A straightforward way to assess the fidelity of a model is to compare the model's results from a decade or two ago with actual observed measurements made after the model's results were published. Williams adds, "We did some simulations in 2007, and now, in 2017, we compared the results to observed changes 10 years later. We found that the models predicted the temperature changes we are seeing now. Just plot the data points on the graph." Another striking result was the human impact on climate. Scientists have demonstrated that when human influences such as increased concentrations of greenhouse gases are deliberately excluded from the models, the resulting simulation predicts much colder temperatures than what is observed today. In fact, no model based on careful representation of physical laws has been able to reproduce the actual observed increase in global temperatures over

recent decades without including those human effects.

Each decade since the 1960s has been warmer than the previous decade. Of the 17 hottest years on record, 16 have occurred since 2001, and the years 2014, 2015, and 2016 have consecutively set record high temperatures. These records are independently confirmed by four world-leading science institutions—NASA, the National Oceanic and Atmospheric Administration, the Japanese Meteorological Agency, and the United Kingdom's Met Office Hadley Centre. Climate models help quantitatively explain the extent of the human contribution to this warming. Readily observable, data-based cause-and-effect relationships also help to explain how human influences are driving other changes, such as melting glaciers and ice sheets, warming oceans, and rising sea levels. Accumulated climate changes are driving what the world is experiencing today—such as seawater regularly flooding streets in Miami Beach, Florida, and Newport News, Virginia, at high tide, and the poleward movement of fisheries—adding credence to projections of future trends. The next generation of climate models promises to help us be even better informed and prepared.

Warming near Earth's surface is shown by both (left) satellite observations and (right) climate models, specifically, for temperature change in the lower troposphere from January 1979 to December 2016. The average of historical simulations performed with 37 different climate models corresponds well with satellite temperature measurements made by Remote Sensing Systems.



Models of an Exascale Kind

The DOE Office of Science launched the Energy Exascale Earth System Model (E3SM) program in 2014, but E3SM actually dates back to a 2007 Grand Challenge award at Livermore, which provided researchers a large amount of time on the Atlas supercomputer. Using Atlas, the team ran a simulation using what was then one of the most detailed coupled models of global climate ever produced. Dave Bader, who heads E3SM, says, “We match the strengths of DOE computational science with existing research. DOE has a mission to understand the consequences of energy production and use, and obviously that includes greenhouse gas emissions. This assessment requires an Earth system model, and E3SM is a DOE model, for DOE missions, running on DOE computers.”

By adding the interactive biogeochemical process by which the climate is linked to plant life and other living organisms, global climate models have evolved into Earth system models. A multi-institutional program combining the efforts of six national laboratories and several other leading scientific organizations, E3SM will run simulations at resolutions of 15 kilometers (whereas Leith’s first model had a horizontal resolution of about 500 kilometers). The model will also be able to “telescope” to a resolution as small as 1 kilometer to focus attention on towns or other small locales. E3SM will also incorporate additional Earth system components such as ice shelves and glaciers that can flow and fracture—processes that are critical to projecting future rates of sea level rise.

As part of the DOE Exascale Computing Project, supercomputer architecture is going through a radical transformation. E3SM will start running on pre-exascale supercomputers but is being designed to run on full exascale platforms. As early as December 2017, E3SM will have completed the first of its many simulations addressing

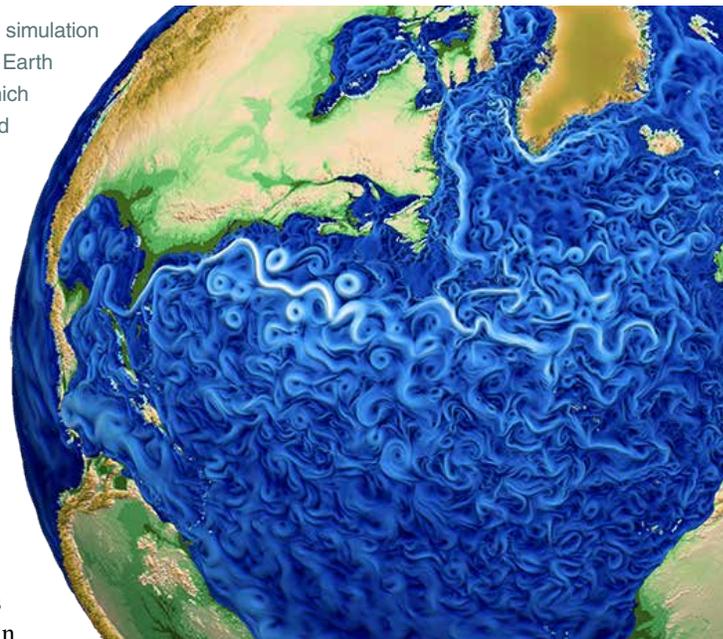
This high-resolution ocean simulation uses the Energy Exascale Earth System Model (E3SM), which divides the globe into a grid with intervals of only 15 kilometers. E3SM will run on the most advanced supercomputers and produce results of unprecedented resolution.

important energy-related questions, such as how the availability of water resources changes over periods as short as decades, how changes in the hydrological cycle will affect energy production, and how changes in heating and cooling will affect the energy needs of infrastructure, business, and the public.

Looking Ahead

The tremendous capabilities Livermore has built in supercomputing have been applied successfully to sustain the nation’s nuclear deterrent and address other national scientific challenges. Those computational capabilities have also advanced research in related mission-critical fields. Livermore’s long, successful history of atmospheric modeling has helped identify and address a broad range of issues in Livermore’s mission space. The improvement of modeling has relentlessly continued, leading to ever more realistic representations of the world. Today, the atmospheric release models used by NARAC deal with scales from local to global as climate models are looking at the world at finer and finer scales.

As with their climate model predecessors, Earth system models cannot be perfectly predictive because of the

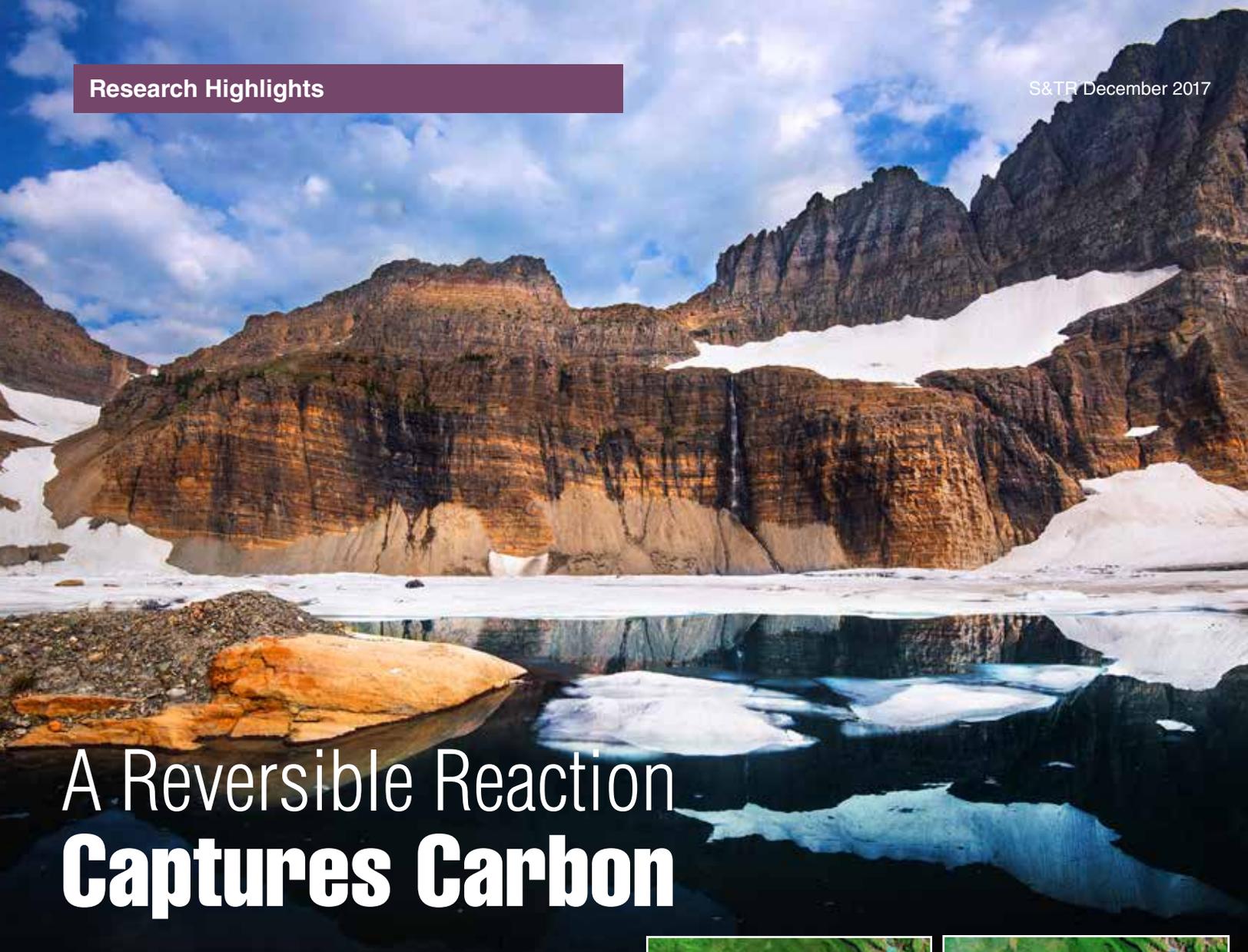


impossibility of simulating every single atom on Earth. Chaos theory also dictates that no model can predict the exact temperature and sky conditions at a given place and time of day even a day from now, let alone 10 or 100 years in the future. However, the emerging capabilities in Earth system modeling will soon provide extraordinary insights into global trends and climate statistics about Earth’s past, present, and future, allowing society to explore what has passed and better predict and prepare for what is to come.

—Dan Linehan

Key Words: atmospheric model, climate change, climate model, Earth System Grid Federation (ESGF), Energy Exascale Earth System Model (E3SM), Intergovernmental Panel on Climate Change (IPCC), Livermore Atmospheric Model (LAM), National Atmospheric Release Advisory Center (NARAC), Nobel Peace Prize, nuclear weapon, Program for Climate Model Diagnosis and Intercomparison (PCMDI), stockpile stewardship, supercomputer.

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A Reversible Reaction Captures Carbon

IN 1910, Glacier National Park in Montana was home to more than 150 glaciers. Now, over 100 years later, that number has fallen to fewer than 30—just one of many signs that global climates are changing. Most scientists believe that human activities are at least partly to blame. Environmental changes that would normally take hundreds of years are happening in the span of a human lifetime, and if that rate continues, scientists see the possible repercussions including increasingly severe weather, wildlife extinction, and higher sea levels.

To combat climate change and other anthropogenic environmental impacts, researchers have identified and analyzed major sources of pollution. One of those sources, and perhaps the most influential and well known, are greenhouse gases.



(top) In Montana's Glacier National Park, the number of glaciers has fallen from 150 to fewer than 30 in the past 100 years. (bottom) Satellite photos show the decrease in glaciers between August 1984 and August 2015. (Images courtesy of the National Park Service and NASA, respectively.)

Greenhouse gases include carbon dioxide (CO₂), methane, nitrous oxide, and fluorinated gases. In the United States, CO₂ constitutes approximately 82 percent of total greenhouse gas emissions, making it a critical factor in environmental research.

CO₂ is released through a variety of human activities, from driving cars to producing electricity, but the biggest concern is CO₂ emitted from large-scale sources such as power plants and industrial sites. In the United States, emissions from such large-scale sources account for more than 50 percent of total CO₂ emissions. In fact, 2.8 billion tons of CO₂ per year are generated by power plants alone. Reducing these emissions is one way to lessen the amount of CO₂ added to the atmosphere, but determining how to reduce that output in actual practice has been problematic (see *S&TR*, May 2004, pp. 20–22; and May 2005, pp. 12–19). Ideally, CO₂ would be separated from power plant flue gas before leaving the smokestack and entering the atmosphere, but this process—known as carbon capture—is prohibitively expensive (see *S&TR*, January 2017, pp. 14–15). Installation of a carbon capture and sequestration system increases power plant costs by 96 percent. In addition, conventional carbon capture technology, which typically uses amine solutions as sorbents, requires low temperature and pressure for CO₂ separation and elevated temperature and pressure for regeneration. This process is energetically inefficient and actually increases the fuel consumption of coal-fired plants by 20 to 40 percent.

In response to this challenge, Lawrence Livermore materials scientist Patrick Campbell and Livermore postdoctoral researcher Maira Ceron Hernandez have developed a new CO₂ separation technology in a Laboratory Directed Research and Development Program project. Their technology relies on the newly discovered phenomenon of a reversible CO₂ reaction in molten hydroxide—a process that can capture carbon efficiently and cost effectively before it leaves the smokestack.

Reversible Reaction

“The reversibility of the reaction is what really makes this technique special. It was not a known phenomenon before,” notes Campbell. The team stumbled upon the potential for reversible CO₂ capture when former Laboratory employee Matt Merrill—the project’s original principal investigator—discovered past research on molten carbonate fuel cells. Campbell explains, “Several groups noticed the carbonate fuel cells were producing CO₂ because water was involved. Matt had the idea to try to reverse CO₂ absorption by recreating those conditions.”

In the scientific community, the reaction whereby molten potassium hydroxide, when combined with CO₂, irreversibly



Current technology for separating carbon dioxide (CO₂) requires drastic pressure and temperature changes in flue gas towers, seen in the center of the photograph. These expensive modifications can consume 25 to 40 percent of a power plant’s energy. New technology developed at Lawrence Livermore could be placed in a plant’s existing heat exchange and separate out hot CO₂ instead of having to cool it first, thereby lowering costs. (Photo courtesy of the National Renewable Energy Laboratory.)

converts to a solid-phase carbonate and water is well known. By experimentally varying temperatures and mixtures of hydroxides, the team discovered that molten hydroxides will reversibly react with CO₂ to form carbonates at temperatures greater than 250°C, as long as enough water is present to balance the hydroxide system. “We found that the amount of water is really important to accomplish reversibility,” says Ceron Hernandez. The discovery, which defied conventional expectations, led the team to try to optimize the molten hydroxide phase with which the CO₂ reacted. The ideal mixture would have a low melting temperature and a high dehydration temperature to keep the carbonates dissolved. The scientists found a lithium–sodium–potassium hydroxide eutectic mixture that fit the bill, with lithium added to increase carbonate solubility and sodium and potassium included to lower the melting point.

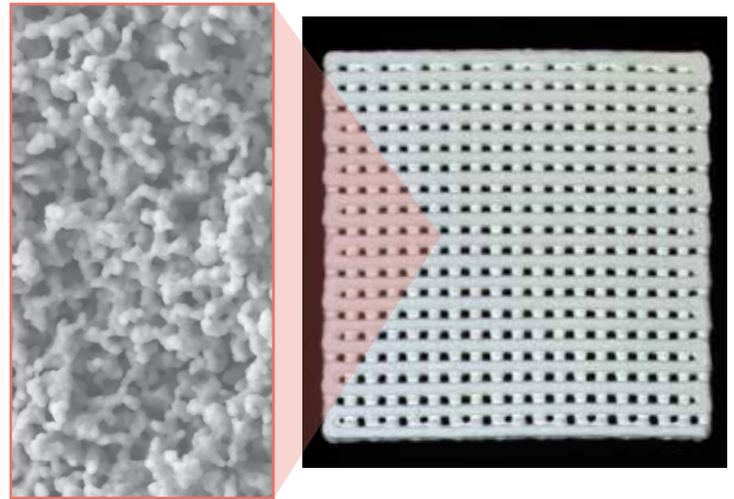
The major costs of traditional carbon separation derive from the drastic pressure and temperature changes needed to absorb and release CO₂. The team therefore endeavored to develop a membrane separation system that would take advantage of the partial pressure gradient between CO₂ on either side of the membrane (high on the flue gas side, low on the sweep gas side)

to naturally drive separation. This membrane would contain the optimized hydroxide mixture which, by reacting with CO_2 to form carbonates, would allow CO_2 to be selectively removed from the flue gas.

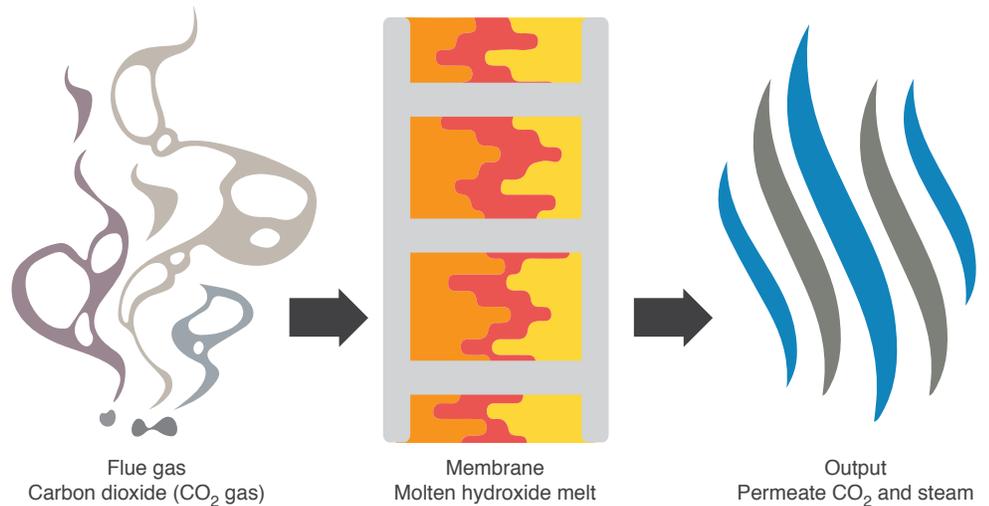
For this process to be successful, the team needed a porous solid support material that could contain the highly caustic hydroxide melt in its pores via capillary forces while withstanding the high flue gas temperatures. Ceron Hernandez discovered such a candidate when she came across a 1992 article illustrating the use of ceramic materials with sodium hydroxide solutions. Using information gleaned from that article, Ceron Hernandez began to test potential ceramic materials and eventually settled on three options—yttria-stabilized zirconia, cerium oxide, and silicon carbide. In a tale reminiscent of Goldilocks and the Three Bears, Ceron Hernandez recounted her experimental process: “For cerium oxide, we couldn’t get the right pore morphology—the pores were too big. With silicon carbide, or commercial foams, not only were the pores too big, but we were also concerned about the lifetime of the material.” After multiple trials, Ceron Hernandez finally found the ceramic material that was just right—the yttria-stabilized zirconia. She further discovered that out of two different zirconia types—fully stabilized and partially stabilized—the partially stabilized zirconia performed the best in the presence of water. She says, “We weren’t sure why, but our theory is that the crystallinity of the partially stabilized zirconia affects the material’s resistance to molten hydroxide.”

With the best ceramic material identified, the team then tackled the challenge of producing the porous membrane. With no suitable membranes commercially available, the team members developed their own. “We were inspired by another Laboratory scientist, Eric Duoss, and his work with additive manufacturing,” explains Campbell. The duo modified existing Laboratory methods for their particular application. Ceron Hernandez adds, “Other Livermore scientists were printing full density ceramic parts using a polymer resin loaded with ceramic particles. We needed the porosity, so we just adapted their methods.” Taking advantage of the Laboratory’s additive manufacturing technology, Campbell and Ceron Hernandez managed to produce porous ceramic materials compatible with additive manufacturing techniques such as direct ink writing and projection microstereolithography.

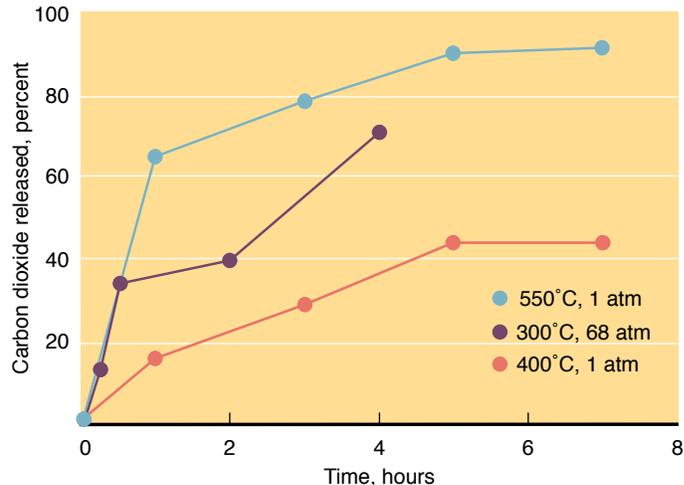
To make the porous membrane, the team put a mixture of ceramic nanoparticles into a polymer resin, turning the material



The ceramic porous material created with yttria-stabilized zirconia is heat and hydroxide resistant and is therefore ideal for use with flue gas temperatures of 300°C to 650°C . The production process is compatible with additive manufacturing techniques such as projection microstereolithography and direct ink writing (DIW). A DIW-produced part is shown.



The dual-phase membrane technology allows CO_2 to be continuously separated. A gas separation membrane containing the optimized molten hydroxide solution held in a porous material selectively turns CO_2 into carbonates. These carbonates are then transported across the membrane by diffusion, which is driven by the difference in CO_2 partial pressure on either side of the membrane. Water—as steam—on the sweep (right) side is critical for enabling the reverse reaction, that is, recovering the captured carbon for storage by converting the carbonate back into CO_2 .



(left) Tests conducted in the tube furnace shown indicate that carbonate is converted to hydroxide upon exposure to humidified nitrogen, releasing CO₂. (right) At atmospheric pressure (1 atm), CO₂ release was highest at 550°C, but by increasing steam pressure to 68 atm, the same conversion could be achieved at 300°C, significantly reducing energy costs.

into a plastic. After sintering and burnout, pores had formed where the polymer had been. “We are sintering to the point where the particles are lightly fused together, leaving residual porosity,” says Campbell. The team surprisingly had no difficulties embedding the hydroxide into the porous ceramic material. Campbell says, “The hydroxide flowed into the pores like water in a paper towel. We didn’t even need a vacuum to pull it through.” With a robust membrane enabling continuous separation, the sequestration technology eliminates expensive infrastructure adjustments, proving both efficient and cost effective. Campbell states, “Because separation occurs at a high temperature, we don’t have to heat the system back up. Our membrane is perfect for placing in a power plant heat exchanger, where steam exists on one side and exhaust on the other, which naturally separates the CO₂. This approach helps lower costs.”

Sequestration and Beyond

Campbell’s and Ceron Hernandez’s technology has wide applications, including more than just large-scale carbon capture and sequestration. Campbell says, “In addition to applying the technology to large point sources of CO₂—such as cement and steelmaking factories—the porous materials themselves have their own applications.” Another unique aspect of the project was the team’s composition, spanning myriad disciplines. Marcus Worsley, a project consultant, has expertise in porous materials; Matt Merrill

is an electrochemist; Sangil Kim, a former Laboratory employee assisting on the project, has experience with high-temperature membrane characterization; and Ceron Hernandez and Campbell are chemists. Swetha Chandrasekaran conducted the direct ink writing. Campbell states, “This is a cross-disciplinary project. You need extensive experience in different areas, and all that experience was needed to make the project successful. The Laboratory was perfect for that because it fosters a unique collaborative environment.”

Moving forward, the duo plans to publish their research and focus on rolling out the technology. They have already filed three records of invention and two patent applications. “The big picture is that we’re all worried about carbon dioxide,” Campbell says. “Currently technology for capturing CO₂ from power plants exists, but the capturing process is very expensive and energy intensive. Our new process provides a more efficient and lower cost CO₂ separation platform.”

—Lauren Casonhua

Key Words: additive manufacturing, carbon capture, Laboratory Directed Research and Development Program, molten hydroxide, porous membrane, reversible carbon dioxide reaction, yttria-stabilized zirconia.

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Investigating Water under Earth's Surface

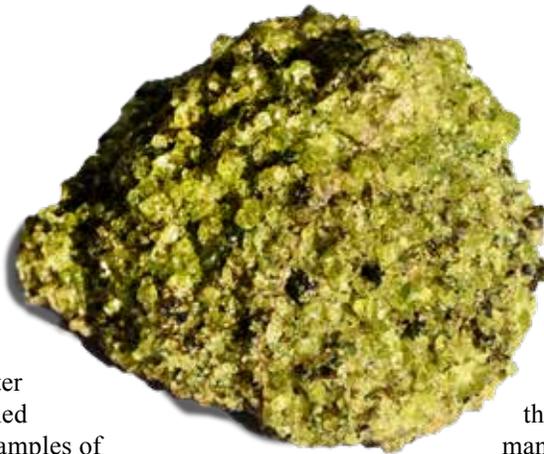
SEEN from space, one of the most striking aspects of planet Earth is its vast oceans, covering more than 70 percent of the surface. Scientists have long wondered why Earth is the only known planet in our solar system to retain such large quantities of liquid water on its surface, and whether the answer could somehow be related to the large amounts of water believed to exist inside minerals formed deep in the planet's mantle. Indeed, samples of minerals transported upwards hundreds of kilometers to the surface through volcanic eruptions have been found to contain water amounting to tens to hundreds of parts per million in weight. (The mantle mostly consists of hot, solid rock and extends from about 30 kilometers below the Earth's surface to the planet's molten outer core, which starts at a depth of roughly 2,900 kilometers.)

The mantle's high pressures and temperatures are believed to force water's constituents—mainly hydrogen ions (protons)—to become trapped inside minerals' crystalline lattices. In particular, the presence of protons is believed to strongly influence the physical and chemical properties of mantle minerals. These hypotheses have been supported by experimental evidence that hydrogen at elevated temperatures and pressures similar to those existing within the mantle could be responsible for regions of relatively high electrical conductivity that have been detected in the mantle.

Livermore materials scientist Wyatt Du Frane and his team have provided new experimental data that demonstrate hydrogen's important contribution to the strong electrical conductivity inside the mantle. The data support the notion that Earth's mantle contains water—and probably a lot of it. The Livermore team included Ben Jacobsen, Peter Weber, Rick Ryerson, and postdoctoral researcher Davide Novella (now at the University of Cambridge). James Tyburczy of Arizona State University also contributed to the research. The work was funded by the Laboratory Directed Research and Development Program.

Water in Olivine

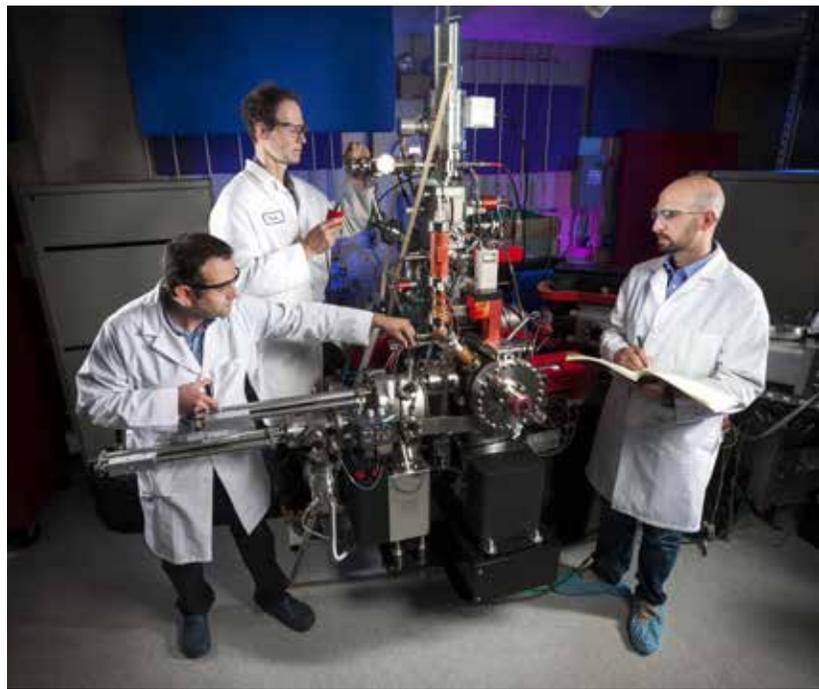
The team conducted experiments at both Lawrence Livermore and at Arizona State on olivine, the predominant mineral in the upper mantle, which reaches to a typical depth of 410 kilometers. Characteristically light green in color, olivine has been found to contain water within its crystalline structure. At higher pressures corresponding to greater depths (down to typically 660 kilometers), olivine transforms to minerals with different crystalline structures known as wadsleyite and ringwoodite, which can hold even greater amounts of water. Recently, a crystal



Olivine, the predominant mineral in Earth's upper mantle, has been found to contain water within its crystalline structure.

of ringwoodite, discovered as an inclusion in a natural diamond, was found to contain about 1.4 percent water.

Du Frane says that scientists have searched for a method to remotely determine the amounts and distribution of water in the mantle. One method is to infer water content from electrical conductivity measurements of the mantle. To do so requires a precise understanding of how hydrogen affects the electrical conductivity of minerals such as olivine under elevated pressures and temperatures. However, a large disparity in published electrical conductivity measurements exists because of the difficulty of conducting such experiments. The Livermore team adopted an alternate approach—studying the diffusion of hydrogen (disassociated from water) under conditions mimicking



The research team—which includes Ben Jacobsen (left), Peter Weber, and Wyatt Du Frane (right)—analyzed samples with Livermore's nanoscale secondary ion mass spectrometer (nanoSIMS), which has a resolution 100 times greater than that of conventional SIMS and is one of the few in the nation equipped to handle geologic samples. (Not shown: Davide Novella, Rick Ryerson, and James Tyburczy.) (Photo by Randy Wong.)

the temperatures and pressures in the upper mantle. The team was then able to use the long-established Nernst–Einstein equations that relate the diffusion of ions to electrical conductivity and thereby infer the contribution of hydrogen (protons) to the mantle’s total electrical conductivity. Using a piston-cylinder press to replicate the pressures and temperatures of the upper mantle, the experiments were conducted on samples of cut single crystals of olivine and focused on determining the diffusion of hydrogen in olivine to calculate its contribution to total electrical conductivity.

Tracking Deuterium

First, a sample of olivine crystal was cut and dried at ambient pressure (101,325 pascals, or 1 atmosphere) and a temperature of 1,300°C to drive out any existing water and fix the distribution of electron holes in the ions and atomic vacancies in the crystal’s structure. Second, the crystal was placed into a liquid water bath and exposed to a pressure of 2 gigapascals (equal to 20,000 atmospheres) and temperatures between 700°C and 900°C to saturate the crystal with hydrogen. Third, under the same temperatures and pressure, the sample was placed into a liquid bath of deuterium (hydrogen atoms each consisting of one proton and one neutron). Deuterium acted as a tracer that could be easily followed as it made its way through the crystal, replacing the existing hydrogen ions. The samples were next brought to room temperature, effectively fixing the diffused deuterium in place.

Du Frane explains that hydrogen diffusion is dependent upon the direction it travels through olivine. Consequently, diffusion coefficients are needed for olivine’s three principal orientations—determined by x-ray diffraction—to accurately calculate the contribution of hydrogen ions to electrical conductivity. To attain the spatial resolution required for simultaneously resolving the multiple diffusion profiles, the team turned to

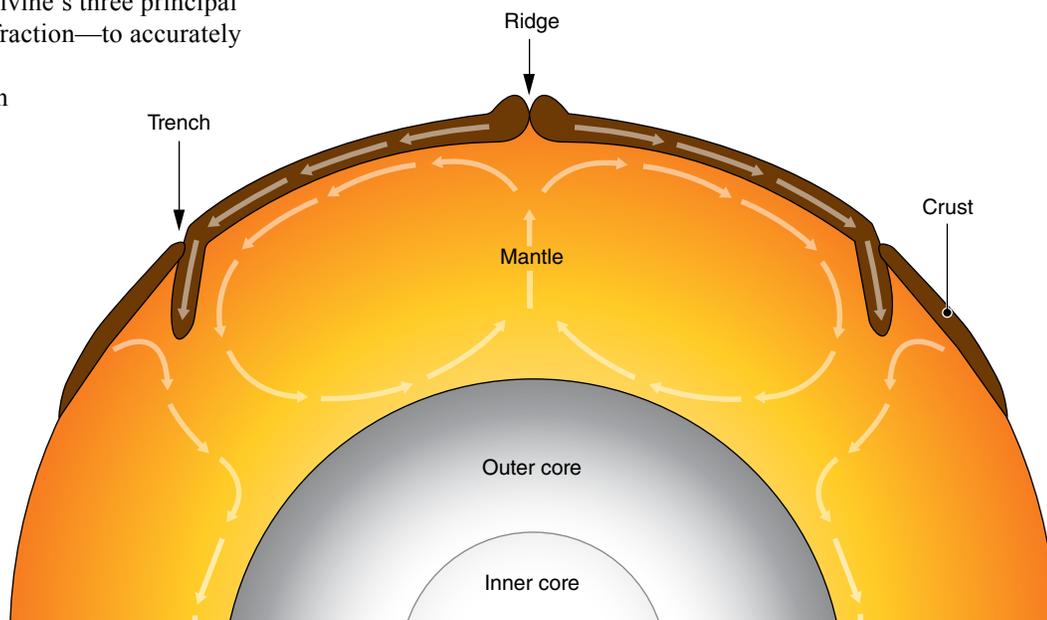
the Laboratory’s nanoscale secondary ion mass spectrometer (nanoSIMS) instrument. NanoSIMS analyzes the composition of solid surfaces and thin films by sputtering specimens with a beam of ions and collecting and analyzing the ejected ions to determine composition down to a spatial resolution of 50 nanometers.

With a resolution 100 times greater than that of conventional SIMS, Livermore’s nanoSIMS is one of the few in the nation that can assess geologic samples. The instrument allowed the team to measure hydrogen diffusion in olivine along the three principal orientations simultaneously, showing that diffusion is highly directional—protons travel approximately 10 times more quickly in the fastest orientation than in the other two. Du Frane says, “Our nanoSIMS instrument not only measures deuterium concentrations but is capable of imaging them, as well.” He adds that the team’s development of the nanoSIMS capability to quantify hydrogen accurately is important because hydrogen’s behavior in materials is critical to many Laboratory research efforts.

Proton Hopping Conducts Current

The measurements showed that concentrations of water in the upper mantle can account for the high electrical conductivity values (10^{-2} to 10^{-1} siemens per meter) that have been reported by other researchers. The protons are believed to be incorporated into olivine’s complex crystalline structure, occupying vacancies (called defects) where other positively charged ions such as iron and magnesium normally reside. The vacancies are coordinated

Hydrogen’s proven role in geophysical processes supports the theory that the crust’s downwelling oceanic slabs and upwelling plumes may continuously recycle water contained in minerals between surface oceans and the mantle.



by surrounding oxygen atoms, which are negatively charged. The protons “hop” from one vacancy to another, conducting current in the process.

Du Frane states, “Our experiments on olivine show that the contribution of hydrogen to electrical conductivity is quite large at the temperatures thought to exist in the mantle.” The experimental results point to hydrogen from water as largely responsible for the physical and chemical properties of olivine and other mantle minerals, including electrical conductivity. The findings suggest that many oceans’ worth of water could be stored inside the mantle at considerable depths. Furthermore, the research is certain to provide a better understanding of water distribution in the mantle because different electrical conductivities can be an effective technique for mapping water distribution.

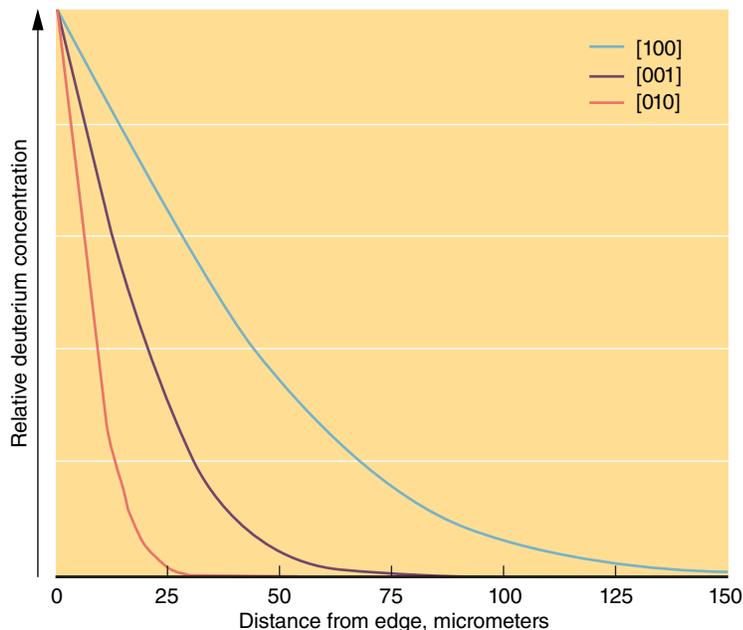
Plate tectonics are the result of deep mantle convections, evident as upwelling plumes and downwelling oceanic slabs. These convections are imaged by seismic tomography, which is similar to ultrasound imaging. Hydrogen is known to alter the physical and chemical properties of olivine and other mantle minerals, so its presence in the mantle would significantly affect large-scale geophysical properties such as plate tectonics, deep earthquakes, and volcanic activity.

“Hydrogen changes all the physical properties of the mantle,” notes Du Frane. For example, the element weakens silicon–oxygen bonds, reduces melting temperature, and moderates the flow of molten materials. Hydrogen’s all-important role in global geophysical processes supports the theory that downwelling oceanic slabs and upwelling plumes at mid-ocean ridges, volcanoes, and hotspots may continuously recycle water between surface oceans and the deep mantle. Indeed, the mantle could contain as much water as all of Earth’s oceans combined.

Understanding Earth’s Origin and Evolution

Du Frane states that a better understanding of present-day hydrogen distribution in Earth’s mantle could also advance scientific understanding of Earth’s origin and evolution, including how our planet has managed to retain its oceans. Livermore’s hydrogen-diffusion technique is sure to help determine the mechanism and rate of proton movement through the crystal lattice structures of olivine and other mantle minerals. With such information, researchers could infer regional water content from geophysical measurements of electrical conductivity.

Du Frane states, “Carl Sagan famously stated we are all made of ‘star stuff.’ If all planets were made from the same star stuff, why are they so different today? Expanding our understanding of the chemistry and physics of mantle minerals will help answer such fundamental questions. Although Mars and Venus exhibit evidence of water in their distant past, Earth is the only planet in our solar



The team measured deuterium diffusion in olivine along the mineral’s three principal orientations, represented as [100], [001], and [010], which correspond to the three different faces of the mineral’s crystalline shape. The results showed diffusion to differ greatly depending on orientation. The graph shows the concentration of deuterium in the crystal of each orientation at a single point in time.

system that has retained its oceans and the only planet known to have plate tectonics. Planets might exist elsewhere in the universe that also possess vast oceans of water. Understanding the evolution of water on Earth therefore informs the possible evolution of other Earthlike planets.” As candidates of exoplanets that could contain surface water, Du Frane cites the recently discovered TRAPPIST-1 system, which consists of seven Earthlike planets 40 light years away. In addition, Jupiter’s moon Europa and Saturn’s moon Enceladus are thought to harbor oceans of water beneath icy crusts. Experiments in the laboratory are bringing Earth’s depths and distant exoplanets into closer focus.

—Arnie Heller

Key Words: exoplanet, hydrogen, Laboratory Directed Research and Development Program, mantle, nanoscale secondary ion mass spectrometer (nanoSIMS), Nernst–Einstein equations, olivine, ringwoodite, tectonic plates, TRAPPIST-1, wadsleyite, water.

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The Dawn of an Optical Revolution

WHAT does the National Ignition Facility—the world’s largest laser system—have in common with a handheld camera? Both rely on precisely calibrated optics—mirrors, lenses, and other components—to direct light toward a target. Industry standards often evolve as researchers strive for better performance and cost effectiveness. In support of the Laboratory’s national security mission and a range of related applications, Lawrence Livermore scientists and engineers are continually advancing optical technology, including materials development and processing methods. (See *S&TR*, April/May 2017, pp. 17–20; July/August 2016, pp. 12–15; and September 2014, pp. 4–12.)

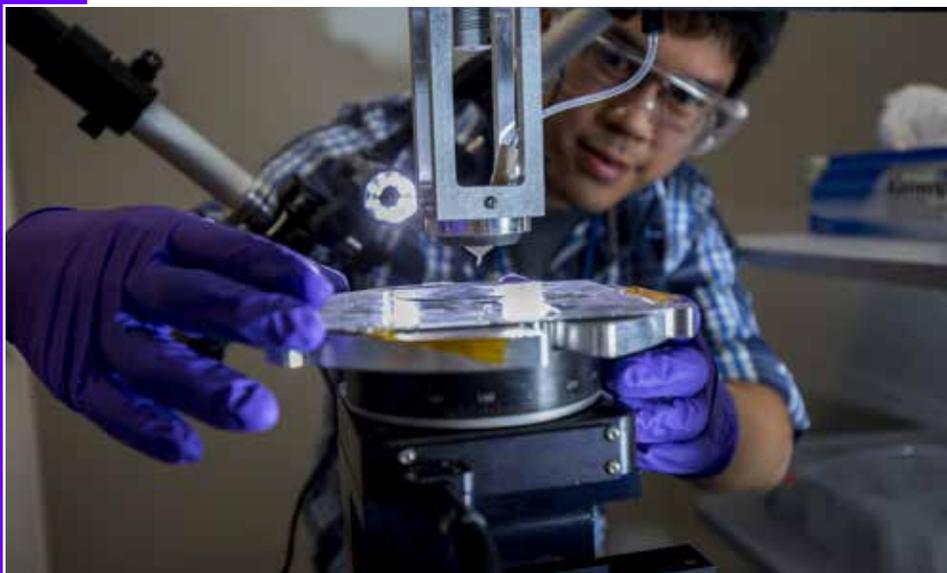
For an optical system of any size, innovations revolve around three variables: size, weight, and power. For example, a typical lens refracts light through its convex shape, which occupies valuable space when combined with other lenses in a series. Changing the compositional or structural properties of a lens can alter its shape, size, weight, performance, and production

cost. Livermore chemical engineer Rebecca Dylla-Spears leads a team exploring new optical designs and fabrication methods. She explains, “With the right technology, we could potentially downsize an optical train to use fewer optics, creating a more compact system.”

In a project funded by the Laboratory Directed Research and Development (LDRD) Program, Dylla-Spears’s team is developing optical components with functionally graded material properties—that is, refractive and other properties resulting from changes to an optic’s composition or structure, not its shape. Such advancement makes use of Livermore’s capabilities in additive manufacturing (AM), also known as three-dimensional (3D) printing. In a breakthrough for AM technology, the team has “printed” optical-quality glass, lenses with a gradient refractive index (GRIN), and gradient-composition laser gain media.

The multidisciplinary team’s goals lie at the intersection of the Laboratory’s leadership in laser technology, optical engineering,

Laboratory engineer Du Nguyen monitors the progress of ink deposition onto a substrate during direct ink writing. (Photo by Jason Laurea.)



Livermore researchers are using additive manufacturing to print a new class of optics, such as this gradient-composition glass optic, shown gripped in a lens-holding tool. (Photo by Jason Laurea.)

advanced materials science, and AM technology. The project spans multiple classes of optics and different AM techniques, notably direct ink writing (DIW). “We’re combining our skills to move rapidly,” says Dylla-Spears. “Learning from other areas of the Laboratory and discovering different approaches to problem solving are important for moving forward.”

Finding the Right Recipe

Besides transparency, next-generation optical glasses will have high-resolution architectures made without a mold. Conventional glass-processing techniques and many advanced manufacturing methods fall short of these goals. For instance, heat-based printing can generate forms by melting and fusing silica (silicon dioxide) powders, but the process leaves the silica filaments vulnerable to thermal stress and can result in nonuniform structures. The LDRD team saw potential in DIW, a mainstay of Livermore’s AM capabilities that provides scientists with

submillimeter precision for many material properties. (See *S&TR*, March 2012, pp. 14–20.) Dylla-Spears states, “We chose DIW because it gives us the most control over composition in three dimensions.”

DIW-printed glass optics present significant challenges at all stages of fabrication. The ink needs to hold its shape, remain stable during printing, and flow at just the right rate to eliminate gaps between print lines. In addition, the printed structure must be mechanically strong to survive shrinkage during thermal treatment—drying, burnout, and sintering. Finally, to achieve the desired optical finish, the glass must withstand polishing without deformation or acquiring new defects. “These processes are dependent on pore and particle size,” notes Dylla-Spears. “Altering ink composition affects the heat treatment process, as well. Cracking is a problem, as are bubbles, or voids, in the glass. If stresses develop during sintering, the piece is ruined.”

Dylla-Spears and colleagues began by using a silica slurry to print glass. This series of experiments proved DIW’s viability for producing silica optics, so the next step was determining how to control the glass’s refractive properties. The team developed a custom ink by combining silica with titania (titanium dioxide), a common glass additive, to form a colloidal suspension that included precursors, binders, and solvents. In a second round of experiments, the inks were blended in a reservoir before extrusion through the nozzle. “By adding titania to silica and refining the process accordingly, we translate the optical prescription of the refractive index to a print prescription,” explains Dylla-Spears.

As the DIW printer deposits the ink on the substrate, the mixture is adjusted at different stages to create the structure's gradient composition in a radial pattern. The finished GRIN lens is a flat disc.

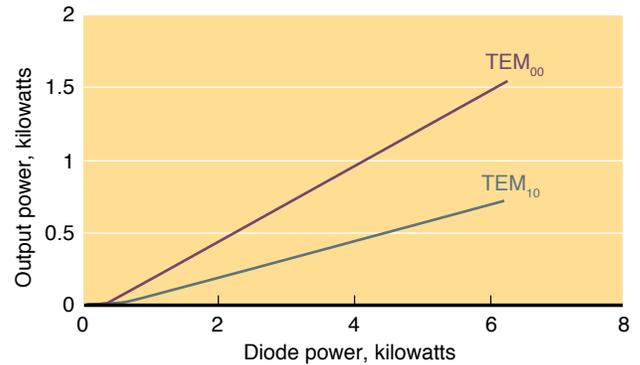
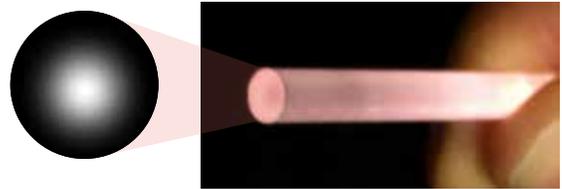
Making the Grade

For decades, gain media—laser rods used to amplify laser energy—have been made from a single crystal of neodymium-doped yttrium–aluminum–garnet (Nd:YAG). However, uniform doping throughout the cylindrical structure leads to inefficiency as energy farther from the central axis of the rod is not extracted. A rod with tailored doping promises better laser efficiency and beam quality but cannot be grown as a single crystal, while manufacturing a rod from two or more parts poses fabrication challenges. As part of the LDRD project, Laboratory physicist Stephen Payne leads development of a cylinder of transparent Nd:YAG by DIW. Nd-doped and undoped YAG inks are extruded independently. In doped inks, Nd becomes concentrated in the cylinder's core so that the outer cladding remains Nd-free. According to Livermore scientist Nerine Cherepy, energy efficiency comes from this spatial change in the rod's structure.

Ink composition is key to creating a doped rod. The team combines high-surface-area nanoparticles with surfactants and polymers to produce unique shear-thinning characteristics, so that ink viscosity can change during printing. "The ink should flow freely through the nozzle, but afterwards it must gel on the substrate," explains Cherepy. "The particles within the ink are lubricated with surfactant to create a weak bond. Moving through the nozzle temporarily overcomes the bond between particles."

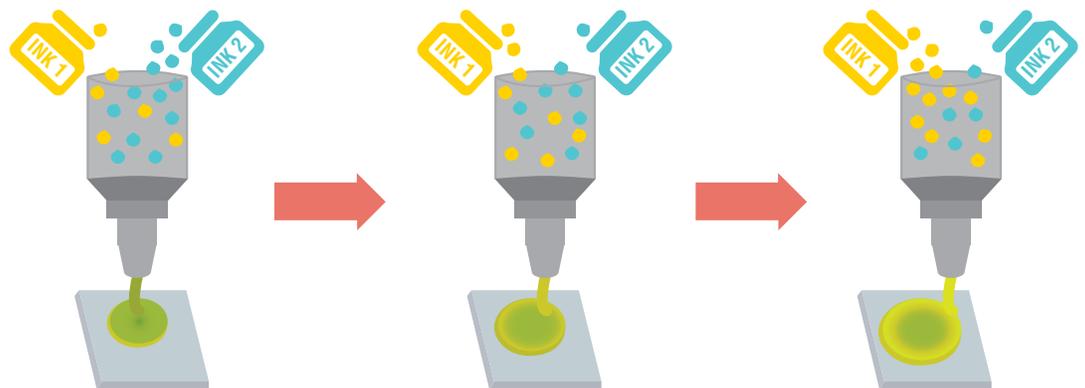
After printing by chemical engineer Tim Yee, the cylinder goes through ceramic processing, which had already proven successful and scalable for other transparent ceramic optics. (See *S&TR*, January/February 2017, pp. 12–13.) The piece undergoes multiple steps—including vacuum sintering and hot isostatic pressing—at different pressures and temperatures. Ceramist Zachary Seeley notes, "Our approach to manufacturing and

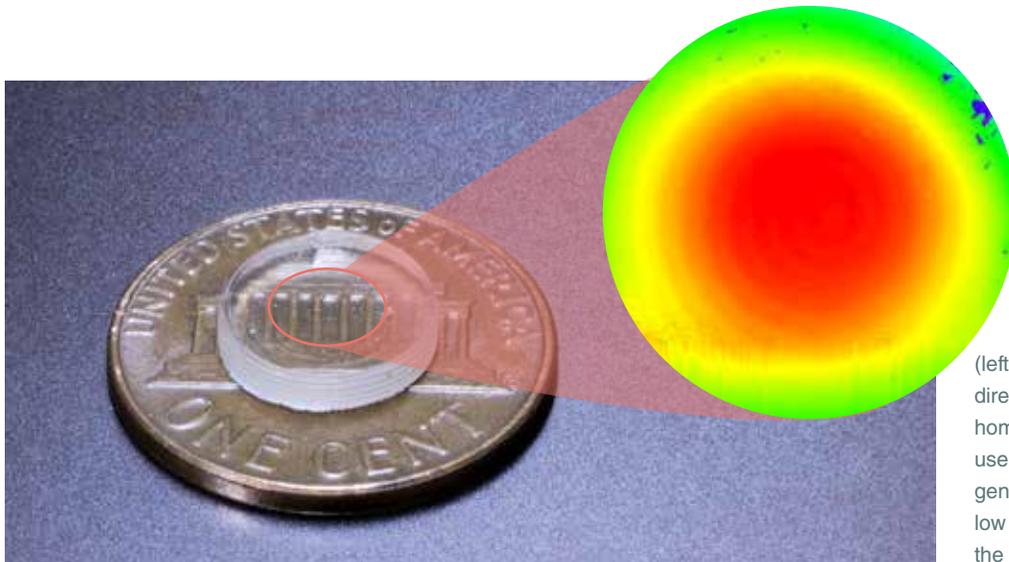
processing should double the efficiency of gain media." Another goal is to create a cylinder with a high-aspect-ratio geometry, where the typical gain medium rod is many times longer than its diameter. Mechanical technologist Scott Fisher has developed ways to support the cylinder during DIW printing. Payne states, "As this technology matures, we will see many new possibilities. Optical components could be printed to design specifications."



(top) A rod of Livermore's tailored transparent ceramic gain medium contains a neodymium-doped core surrounded by undoped cladding. Optimized ink composition ensures uniform light propagation from the rod's center to edge. (bottom) Calculations of the Gaussian beam transverse electromagnetic (TEM) profiles shown illustrate how the graded rod amplifies power more effectively in the higher efficiency TEM₀₀ mode than in the lower efficiency TEM₁₀ mode.

Livermore researchers create gradient-composition optics with direct ink writing technology and tailored inks. Changing the proportions of the mixed inks while printing alters the refractive index, producing a refractive-index gradient indicated by the color gradient in the printed lens. (Subsequent lens-crafting steps omitted.)





(left) A gradient refractive index lens printed with direct ink writing is shown. (right) To determine the homogeneity of the lens's refractive index, researchers use phase-shifting diffraction interferometry to generate a map of the bulk material. The high (red) to low (blue) refractive indices of this piece correspond to the gradient pattern.

Quality Matters

Although gradients are visible in the team's 3D-printed structures, proof comes from refractive evaluation. The quality of a functionally graded lens is determined by homogeneity in its refractive index—that is, the consistency of light passing through. Using phase-shifting diffraction interferometry and correcting for any surface-shape effects, the LDRD team can quantify the lens's bulk material properties. Compared to commercial glass materials, Livermore's GRIN lens exhibits industry-standard density and approaches the chromatic dispersion and spectral absorption of conventionally manufactured silica–titania optics. Moreover, this technique has shown that printed glass can rival commercial silica glass in homogeneity of optical index. Dylla-Spears notes, "With control over material composition, the opportunities to modify other optical and material properties, such as absorption and thermal conductivity, are wide open."

Optical diagnostics confirm that the team's specially doped gain media can meet expectations. Scatterometry measures light traveling end-to-end through the rod, while interferometry measures refractive index. However, Nd doping introduces a slight change to the rod's refractive index. "To compensate for this change and obtain uniformity throughout the rod, we tune the composition of the outer cladding with lutetium doping," explains Seeley.

Just Getting Started

In another parallel effort, the LDRD team is using large-area projection microstereolithography to fabricate gradient-composition lattices for mirror components. The technique is ideal for manufacturing 3D structures with extremely fine features (see *S&TR*, January/February 2016, pp. 14–15). Optical mirrors

are traditionally made from solid glass or metal, which is shaped before the surface is polished or coated for reflection. The larger the mirror, the more susceptible it is to problems associated with weight reduction, such as weakened support structures. By using AM in mirror fabrication to develop ultralight, ultrastiff microlattices, Livermore engineers can specify functional gradients to optimize the lattice supports. Postdoctoral researcher Nik Dudukovic explains, "We can control the global and local stiffness of the support structures by increasing the lattice density at points where high stresses are anticipated while also minimizing the lattice's overall density and weight." In addition to aerospace applications, Dudukovic says lightweight mirrors can potentially improve dynamic performance and reduce the power and size requirements for motor components in fast-scanning optical systems.

As Dylla-Spears's team advances the manufacturing possibilities for optical components, project goals include developing additional ink blends, scaling the 3D-printed pieces to larger sizes, and further refining multistep AM processes. "We're aiming for optics design and experimental efforts to go hand in hand," states Dylla-Spears. "The potential exists to revolutionize optical system design."

—Holly Auten

Key Words: additive manufacturing (AM), direct ink writing (DIW), functionally graded optical material, gain medium, gradient refractive index (GRIN), Laboratory Directed Research and Development (LDRD) Program, large-area projection microstereolithography, National Ignition Facility, neodymium-doped yttrium–aluminum–garnet (Nd:YAG), optics, phase-shifting diffraction interferometry, refraction, silica (silicon dioxide), three-dimensional (3D) printing, titania (titanium dioxide).

For more information contact Rebecca Dylla-Spears (925) 422-1700 (dyllaspears1@llnl.gov).

In this section, we list recent patents issued to and awards received by Laboratory employees. Our goal is to showcase the distinguished scientific and technical achievements of our employees as well as to indicate the scale and scope of the work done at the Laboratory. For the full text of a patent, enter the seven-digit number in the search box at the U.S. Patent and Trademark Office's website (<http://www.uspto.gov>).

Patents

Device and Method for Treatment of Openings in Vascular and Septal Walls

Pooja Singhal, Thomas S. Wilson, Elizabeth Cosgriff-Hernandez, Duncan J. Maitland
U.S. Patent 9,670,308 B2
June 6, 2017

Compact Insert Design for Cryogenic Pressure Vessels

Salvador M. Aceves, Elias Rigoberto Ledesma-Orozco, Francisco Espinosa-Loza, Guillaume Petitpas, Vernon A. Switzer
U.S. Patent 9,677,713 B2
June 14, 2017

Nanolipoprotein Particles Comprising Hydrogenases and Related Products, Methods and Systems

Sarah E. Baker, Brett A. Chromy, Paul Henderson, Paul D. Hoeprich, Jr.
U.S. Patent 9,688,718 B2
June 27, 2017

System and Method for Measuring Fluorescence of a Sample

Vincent J. Riot
U.S. Patent 9,689,799 B2
June 27, 2017

Developing Bulk Exchange Spring Magnets

Scott K. McCall, Joshua D. Kuntz
U.S. Patent 9,691,545 B2
June 27, 2017

High-Performance Rechargeable Batteries with Fast Solid-State Ion Conductors

Joseph C. Farmer
U.S. Patent 9,692,078 B2
June 27, 2017

Awards

Mechanical engineer **Rose McCallen** has been named a **2017 Distinguished Alumni** by **California State University (CSU) at Chico**. One of eight alumni recognized, McCallen was honored by the university's College of Engineering, Computer Science, and Construction Management. McCallen has long remained active with CSU Chico, serving on the advisory board of the university's Department of Mechanical and Mechatronic Engineering and Sustainable Manufacturing. She also participates in its annual "Alumni in the Classroom" presentations and on-campus workshops to assist students applying for government internships and fellowships. McCallen has led a variety of projects during her 35-year career at Livermore. In her current position, she performs program development and university relations work for Livermore's Weapons and Complex Integration Principal Directorate.

Mathematician **Carol Woodward** became the first Livermore employee named a **fellow** of the **Society for Industrial and Applied Mathematics (SIAM)**, in recognition for her work developing mathematical algorithms and software for faster and more accurate simulations of complex physical phenomena. Woodward is a project lead of the Suite of Nonlinear and Differential/Algebraic Solvers (SUNDIALS) project and has developed algorithms for applications as diverse as subsurface flow, particle transport, fusion, climate, supernovae, and materials science. Only 28 SIAM fellows were selected this year, and Woodward was one of only two from Department of Energy laboratories.

Kathleen Shingleton of the Radiation Protection functional area in the Environment, Safety, and Health (ES&H) program has been appointed as a **member** of the **National Council on Radiation Protection and Measurements (NCRP)**. Shingleton is the radiation

safety technical lead at Livermore and has held various technical and managerial positions related to ES&H. She served as secretary and president of the American Academy of Health Physics and as treasurer and member-at-large of the Health Physics Society. NCRP seeks to formulate and widely disseminate information, guidance, and recommendations on radiation protection and measurements that represent the consensus of leading scientific thinking. Shingleton recently retired in June after 38 years of contributions to the Laboratory.

Livermore physicist **Félicie Albert** received the **2017 Katherine E. Weimer Award** from the Division of Plasma Physics (DPP) of the **American Physical Society**. Albert was recognized "for pioneering development and characterization of x-ray sources from laser-wakefield accelerators and Compton scattering gamma-ray sources for applications in high-energy-density science and nuclear resonance fluorescence." The award established by DPP recognizes and encourages outstanding achievement in plasma science research by a woman physicist in the early years of her career.

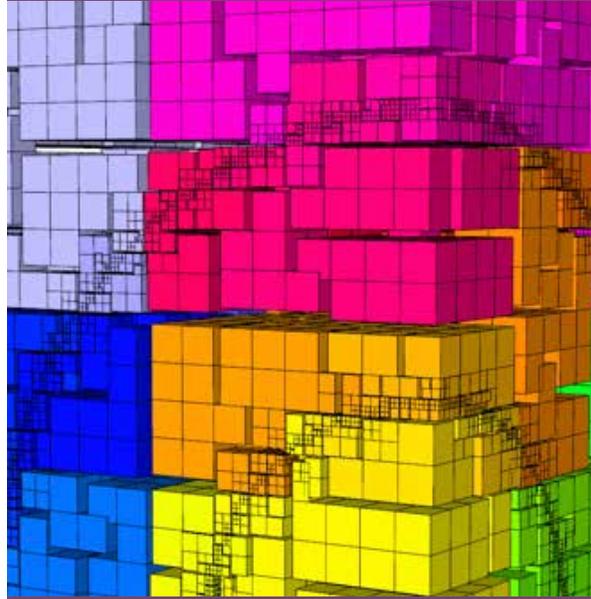
U.S. Marine Corps veteran **Destiny Goddu**, who works as a mechanical engineering technician at the National Ignition Facility, was named the **16th Assembly District's Veteran of the Year** by Assemblywoman Catherine Baker during a ceremony at Las Positas College. Goddu stood out among veterans in the area not only because of her distinguished military service but also her work with other student veterans at Las Positas, where she recently received her associate degree in engineering technology. Goddu earned her degree through the Veterans to Technology program, a collaboration between Lawrence Livermore, Las Positas College, and the Alameda County Workforce Investment Board.

The Atmosphere around Climate Models

The founding of the Laboratory led to a long, successful history of atmospheric science and climate modeling. The Laboratory's continued emphasis on computation prowess has allowed researchers to make advances vital to national security. Aside from the complex computing requirements needed for nuclear weapons development, computerization has also been ideal for gaining a much better understanding of the atmosphere. In the 1960s, former Manhattan Project researcher Cecil "Chuck" Leith created the world's first global atmospheric model, which was also the first to be animated. Through the 1970s and 1980s, Livermore ran studies using climate models. Also, atmospheric chemistry modeling helped to solve the hole in the ozone layer, while atmospheric release modeling helped to safeguard citizens from catastrophes such as Chernobyl's nuclear accident. In 1989, Livermore took the lead in the Program for Climate Model Diagnosis and Intercomparison (PCMDI), work that contributed to the 2007 Nobel Peace Prize. Livermore's continual advancements in supercomputers for weapons programs also enabled more complex and higher performing climate models. In 2014, the Department of Energy (DOE) launched the Energy Exascale Earth System Model (E3SM), which will operate on DOE's latest exascale computers. E3SM will have unprecedented resolution, globally to 15 kilometers and telescoped to 1 kilometer. Earth system modeling provides extraordinary insights into the complexities of how the world works.

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Ambassadors of Code



Livermore's culture of open-source software development strengthens Laboratory programs with an engaged user community.

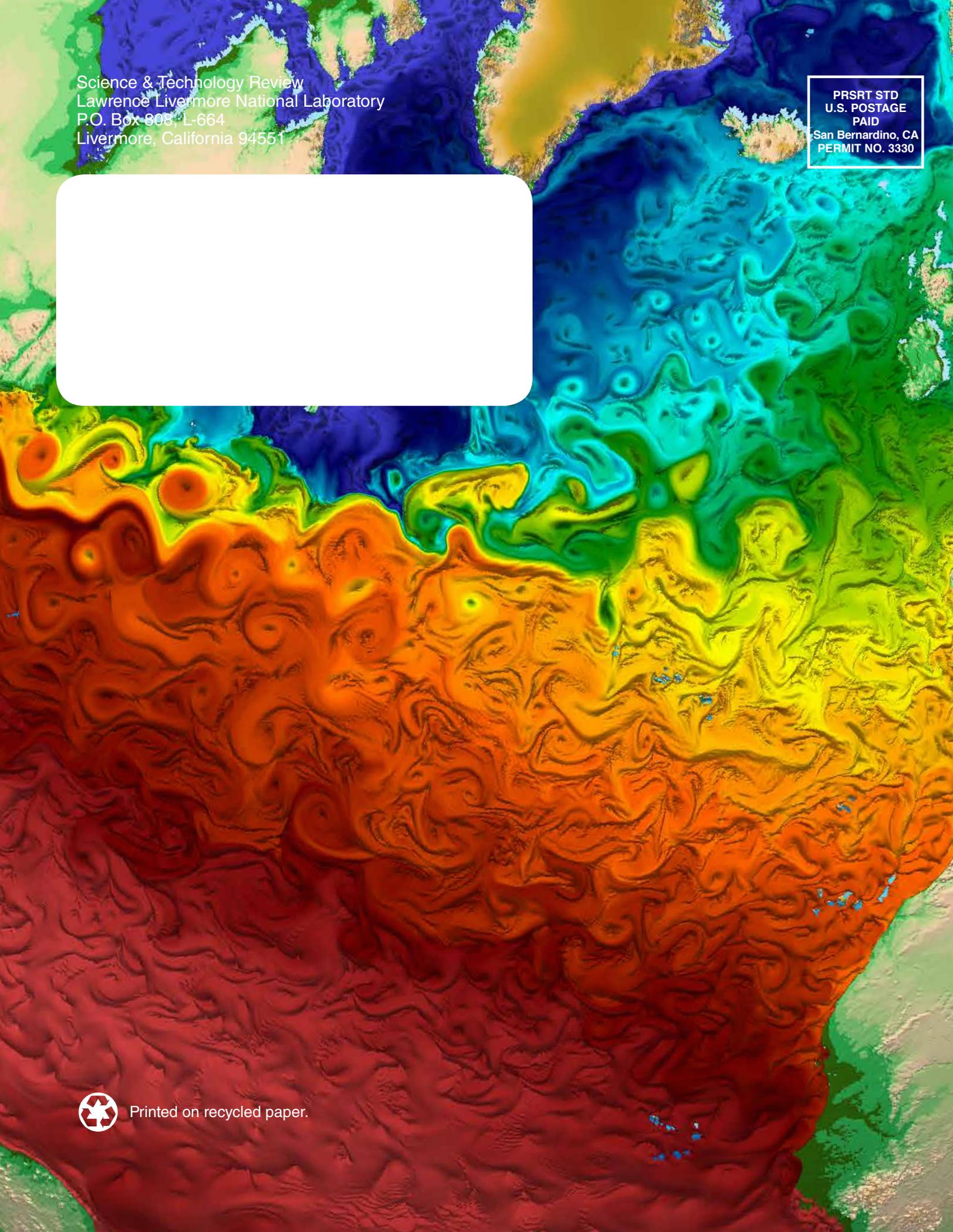
Also in January/February

- *Recent Livermore research advances technology to store hydrogen in solid materials for transportation and industrial applications.*
- *A simulation capability developed at the Laboratory models mechanical waves in the atmosphere and ground, shedding light on energetic events, including earthquakes and terrorist blasts.*
- *A Livermore-developed biodetection system aids researchers in identifying potential pathogenic risks aboard the International Space Station.*

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